Emissions from Domestic Heating Oil Combustion

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INTRODUCTION

During the last ten years, in which the protection of the environment and
expecially our air has become a major national concern, the automobile has received
most attention. As federal controls limiting the emissions from the automobile have
been legislated and gone into force, and federal ambient air quality standards were
adopted, the diesel engine and large stationary steam generators have also come
control by virtue of federal law. All combustion processes are potential sources
of air pollution and all of the major fuel consuming units except one are now
covered by federal emissions regulations. The one exception is the residential
heating unit. Since a substantial share of all petroleum is consumed in residential
use particularly in the winter, we felt it important to study this potential source
of air pollutants. Previous work reported in the literature (1-7) studied effects
of equipment design and operating conditions. Our own interest in this study was
to look at the effect of fuel composition on emissions. This paper summarizes the
more important results of this study.

EXPERIMENTAL

The pollutants measured in this study can be divided into gaseous
emissions, smoke and particulates, and polynuclear aromatic hydrocarbons. Among
the gaseous emissions direct measurements were made of carbon monoxide, total
hydrocarbons, and nitrogen oxides. Carbon monoxide was measured with a non-
dispersive infrared analyzer which on its most sensitive setting was calibrated to
read in the range of 0-250 parts per million (ppm). Total hydrocarbons (HC) were
measured by flame ionization. Both the analyzer and the sampling lines were
heated to keep the sample temperature at no less than 270°F (135°C) to minimize
losses of the higher boiling hydrocarbons. The most sensitive range of the ana-
lyzer was 0-10 ppm HC as methane. Nitrogen oxides (NO_x) were measured with a
chemiluminescence analyzer. The most sensitive range of the analyzer was 0-2.5
ppm.

A parameter of long standing in the heating oil business to characterize
combustion is smokiness. The Bacharach smoke spot measurement is the universally
used technique for measuring the degree of smokiness. This technique was used in
this study to measure smoke at steady state conditions. For continuous measure-
ment of smoke, the Von Brand smoke meter was used. This latter is particularly
useful for measuring the smoke during burner startup and shutdown. In both tech-
niques, a sample of the flue gas is pulled through a filter paper and the result-
ing smoke spot or trace can be compared to a standard scale going from zero smoke
to a number 9 smoke.

Mass particulate emissions were measured using the EPA technique speci-
fied for stationary sources for which emissions regulations exist. An isokinetic
sample of flue gas is drawn from the breech of the furnace through a heated probe
and then a filter is used to catch the solids contained in the measured volume
of sample gas. The quantity of particulates trapped on the filter is determined
gravimetrically.

No standardized method for sampling polynuclear aromatic hydrocarbons
(PNA's) exists at present. Our approach has been to withdraw continuously a

flue gas sample from the furnace breech under isokinetic flow conditions. Isokinetic sampling is used since PNA's may be adsorbed on the particulates contained in the flue gas. The sample probe is not heated except by the flue gas itself. The sampled flue gas passes directly from the probe into a series of four glass impingers (See Figure 1). The impingers are immersed in an ice bath and serve to condense as well as trap the PNA's. By the time the flue gas leaves the last impinger its temperature is about 35°F. A small pore size ($\sim 0.2 \mu m$) filter follows the impinger train to trap any particulates that may be carried through the impinger train. The filter is maintained at about 50°F by the chilled flue gas sample. The sample recovery consists of collecting the condensate from the impinger train, the filter itself, and the acetone wash of the probe, impingers and filter housing. PNA's and other organics are extracted from these three separate parts of the sample using cyclohexane. Analysis of PNA's is done by a combined gas chromatography – UV absorption technique. PNA's are separated into individual fractions on a GC column, and each fraction is analyzed by UV absorption to determine the quantity of the specific PNA contained in the fraction. To account for sample handling and analysis losses C^{14} tagged benzo(a)pyrene and benz(a)anthracene are added to the three parts of the sample before extraction. PNA losses during the analytical procedure are determined from the measured loss of the two radioactive trace components. A detailed description of the analytical procedure is given elsewhere (8).

To determine burner operating conditions, additional measurements were made for CO_2, oxygen, flue draft, flue gas temperature, and fuel flow. Flue gas volumes were calculated from measurement of fuel flow and excess air assuming complete combustion of fuel. Actually measured flue gas flows differed from such calculated flows by no more than 3%. The unit on which the measurements were made was a commercially available hot air furnace with a maximum heat input of 119,000 BTU/hr. The furnace was fired with a conventional high pressure gun burner at a nominal firing rate of 0.75 GPH.

RESULTS AND DISCUSSION

Gaseous Emissions

Figure 2 shows CO emissions as a function of equivalence ratio (E.R.). The equivalence ratio is the ratio of actual air to that required for stoichiometric combustion of the fuel. An E.R. of 1.6 which is typical for field installations, is equivalent to the use of 60% excess air. Results are shown for three fuels differing in gravity, aromatics, and final boiling point. The typical fuel is the only one classified as a No. 2 fuel oil, with the kerosene having a much higher API gravity and the low gravity fuel being too low in gravity. The emissions furthermore are given for two operating conditions, at steady state and for a 5 minute burn – 5 minute off cycle. The results for cyclic operation are time-averaged from the point at which the burner starts to a point 30 seconds after shutdown. The latter is included since the CO emissions tend to be higher immediately after burner shutdown. The CO emissions under steady state conditions are very low even during the relatively fuel rich and smoky operation that is obtained at equivalence ratios lower than 1.4. In fact in the normal operating range to be found in the field (1.5 to 2.0 E.R.), the carbon monoxide in the flue gas is at a lower concentration than in the laboratory combustion air. Even under cyclic operation the CO is low when 40% or more excess air is used. In terms of fuel effects, the high gravity, low final boiling point kerosene gives somewhat lower CO emissions, particularly as less excess air is used. From our point of view it was not considered important to investigate the causes for the observed behavior since under normal operating conditions the CO emissions were low with all three. Differences between fuels occurred under burning conditions which would not normally be used because of smoke limitations.

Figure 3 shows emissions ot total hydrocarbons for the same conditions and fuels as previously given for CO. The concentration of hydrocarbons in the flue gas like that for CO is very low, usually less than that contained in the laboratory combustion air except during a short period after startup and after shutdown. Unlike the behavior of CO, under cyclic conditions the hydrocarbons increased at very high excess air levels. As the air velocity tended to become very high, ignition became erratic and in the extreme case the flame would alternately extinguish and reignite for a few seconds at the beginning of the burning cycle. As is clear from Figure 3, there is no effect of fuel composition on hydrocarbon emissions.

Both at steady state and under cyclic conditions, the nitrogen oxide emissions were relatively insensitive to either equivalence ratio or fuel composition. At steady state, emissions averaged about 80 ppm. For the five minute on-five minute off cycle, time-averaged emissions were about 70 ppm.

Smoke and Particulate Emissions

A number of states and localities in the U. S. have laws on the maximum allowable smoke in the flue gas. Smoke behaves much like CO and hydrocarbons in that there is a peaking of the smoke as the burner starts up. As combustion proceeds and the temperature in the combustion zone rises, the smoke decreases. Immediately upon burner shutdown, the smoke in the flue gas again increases to a peak and then drops off to zero as the furnace is swept by ambient air. Startups and shutdowns are not very repeatable in terms of smoke emissions even with the same fuel. The effect of fuel composition on smoke is therefore more clearly seen at steady state operation. Figure 4 shows the Bacharach smoke number as a function of equivalence ratio for four different fuels. It is clear from the figure that there is a difference in smoke number from the four fuels when operating at higher than trace smoke conditions, i.e. less than 70% excess air. A cross plot of smoke number, at for example 50% excess air, against final boiling point shows an excellent linear correlation (Figure 5). Direct substitution of fuels with differing backend volatility could therefore affect the smokiness of combustion. On the other hand these results also illustrate that smoke-free combustion is possible even with fuels having final boiling points substantially higher than found in present No. 2 heating oils, if the excess air is adjusted for the fuel.

As far as domestic heating units are concerned, the smoke number is the only way by which particulate emissions are being characterized. As has been mentioned there do exist federal regulations on mass particulate emissions for very large capacity steam generators. To determine compliance with the regulations, the EPA prescribed a technique to be used for measuring mass particulate emissions. Results of the particulate measurements are given in Figure 6.

Most particulate measurements in our study were made by the EPA procedure. In a limited number of tests, flue gas was sampled in a diluted stream and some measurements were made with a multistage impactor. These measurements are also included in Figure 6. The results shown are for the same fuels for which smoke numbers were given. In addition the figure contains emissions at steady state and for the usual 5 minute on - 5 minute off cycle. Mass particulate emissions are given as a function of smoke number. Most of the measurements were made with a typical heating oil. There is a correlation of particulate emissions with smoke which is quite pronounced at the higher smoke numbers. For operating conditions typical in the field, trace to about a number 4 smoke, the emissions at trace smoke can be just as high as at number 5. Published results of particulate emissions from a field survey of domestic oil heated units also showed no correlation of smoke number with mass particulate emissions (6). The smoke number therefore is influenced not only by mass particle loading of the flue gas but also by the nature of the particles and the particle size distribution. Variations of particulate emissions with operating conditions, i.e. cyclic vs. steady

state, and with different fuels are at a level which is less than the repeatability of the measuring procedure. Unless the smoke becomes very high, mass particle emissions from the gun burner are in the range of 1 to 2 lbs. per 1000 gallons of fuel even with substantial changes in fuel and operating conditions.

Polynuclear Aromatic Hydrocarbons

In the years since polynuclear aromatic hydrocarbons have been identified in the atmosphere, a great many studies of emissions from various sources have been reported in the literature (9). In recent times such studies have concentrated on the automobile engine. Though considerable experience has been accumulated in the experimental approaches to PNA collection one important problem still remains to be solved. That problem is the loss of PNA species during sampling. Although these compounds are easily condensed, they are relatively volatile and easily oxidized. In those parts of the sampling system which are at significantly higher than room temperature the chance for loss is very great. Attempts to quantify such losses in PNA measurements from automobiles (10) by injection of radioactive species into the gas stream sampled, have indicated that under certain conditions, substantially more than half of the reactive PNA's may be lost during sampling. Yet the techniques used to estimate losses raise nearly as many questions as are answered. Our approach to estimate losses consisted of doping the sampling train, exclusive of the probe itself, with known quantities of non-radioactive benzo(a)pyrene and benz(a)-anthracene and then making a normal sampling run. The level of doping was twenty to fifty times the amount of BaP and BaA normally collected in a run. The recoveries measured were 57% for BaP and 46% for BaA. For these two very reactive components perhaps only half of the quantity of each constituent is recovered by the sampling system. As was mentioned previously, losses during the analytical procedure itself were routinely accounted for. In the discussion to follow PNA results reported are those actually measured. They are not corrected for the possible sampling loss described above. Three different types of fuels were run and analyzed for PNA in the fuel and in the flue gas. Results of emissions and fuel aromatic content are shown in Table 1.

TABLE 1

PNA EMISSIONS FROM HEATING OILS
(Lbs./1000 Gals.) x 10^5

	Kerosene		Typical		Low Gravity	
	Fuel	Flue Gas	Fuel	Flue Gas	Fuel	Flue Gas
Pyrene	550	0.8	19,900	6.2	5,700	6.5
Benzo(a)pyrene	12	0.2	190	0.6	124	1.2
Benz(a)anthracene	29	0.04	1,380	0.2	6,340	1.7
Chrysene	110	0.1	3,700	0.2	24,200	0.4
Triphenylene	66	0.2	2,300	0.6	10,100	1.0
Fuel Aromatics - %	13.2		37.1		46.1	

The analytical technique used was able to identify eleven species of PNA's. Results however are reported only for those five species which were consistently found in measurable quantities. In PNA studies from automobiles it had been reported that exhaust emissions were dependent on the aromatic content of the fuel (11-13). As Table 1 shows the three fuels had a big range in aromatic components as well as in fuel PNA content. Looking at benzo(a)pyrene, the differences in emissions between the three fuels are not statistically significant (standard deviation = 0.66), so that the effect of the very large change in aromatic content of the fuel influences the emissions at least of this component to a relatively small extent. As far as BaA is concerned the change in aromatics and PNA content in going from the kerosene to the typical heating oil did not produce a statistically different emission result. Increasing the BaA content of the fuel still further, i.e. moving from the typical to the low gravity fuel, with a relatively small additional increase in aromatics did show a significant increase in BaA emissions though the level is

still quite low. This points to fuel PNA content as influencing emissions more strongly than fuel aromatics. To look at the influence of fuel PNA content, the typical heating oil was doped with pure BaP and BaA without significantly changing other properties.

TABLE 2

EMISSIONS FROM TYPICAL HEATING OIL
(Lbs./1000 Gals.) x 10^5

	As Is		Doped 1		Doped 2	
	Fuel	Flue Gas	Fuel	Flue Gas	Fuel	Flue Gas
Benzo(a)pyrene	190	0.6	1,210	3.6	3,230	4.2
Benz(a)anthracene	1,380	0.2	2,420	0.6	4,800	0.4

The results of the BaP make it clear that increasing the fuel BaP content does increase the level of BaP found in the exhaust. Exhaust BaA on the other hand appears to be less sensitive to BaA level in the fuel. In order to see if significant generation of PNA's occurs in the combustion system the typical heating oil was doped with high boiling aromatics from still bottoms. These heavy fractions contained both PNA's as well as aromatic species in the range of C_{10} to C_{16}.

TABLE 3

EMISSIONS FROM TYPICAL FUEL DOPED WITH HEAVY AROMATICS
(Lbs./1000 Gals.) x 10^5

	Fuel	Flue Gas
Pyrene	47,400	9.4
Benzo(a)pyrene	3,440	<4.5
Benz(a)anthracene	3,700	0.3
Chrysene	5,380	0.3
Triphenylene	4,130	0.9

The results for BaP and BaA are comparable to those of the typical heating oil doped with pure BaA and BaP. The presence of so-called precursors for PNA formation did not show increases in PNA emissions that would not be expected simply from the PNA content of the doped fuel. Regressing the emissions results of the "typical" fuel against the PNA content of the fuel in the normal as well as various doped conditions, allows one, if only approximately, to extrapolate to a zero PNA content. The emissions at this zero intercept should be those which are synthesized in burning that fuel (37% aromatic content). Although these data are scattered, they indicate that even with high aromatics content in the fuel, PNA formation is not significant (about equivalent to that shown from kerosene or less than 0.5 x 10^{-5} lbs./1000 gals.) and PNA's found in the flue gas are those which survive from the fuel.

Survival of fuel PNA's is very low as shown below.

TABLE 4

RATIO OF FLUE GAS PNA TO FUEL PNA

Pyrene	0.02 – 0.05%
Benzo(a)pyrene	0.1 – 0.3%
Benz(a)anthracene	0.03%
Chrysene	0.002%
Triphenylene	0.01 – 0.02%

These numbers first show that PNA's contained in the fuel are most effectively

destroyed. This is not unexpected in view of the low emissions of hydrocarbons
and CO. Secondly, these numbers would permit reasonable estimates of the magnitude
of PNA emissions from heating oil combustion if the fuel PNA content is available.

CONCLUSIONS

From the results obtained in this study, a number of conclusions regard-
ing emissions from the domestic high pressure gun burners are evident. First, in
the range of practical operating conditions there is no significant effect of fuel
composition on the emissions of carbon monoxide, total hydrocarbons, nitrogen
oxides, and mass particulates. Second, at a given excess air level an increase in
the final boiling point of fuel leads to higher smoke. However, with sufficient
excess air, even fuels with very high final boiling points can be burnt essential-
ly smoke free. Third, emissions of polynuclear aromatic hydrocarbons appear to be
primarily dependent on the PNA content of the fuel. It is unlikely, however, that
differences in exhaust PNA's are measurable over the range of PNA's found in No. 2
fuels in the field.

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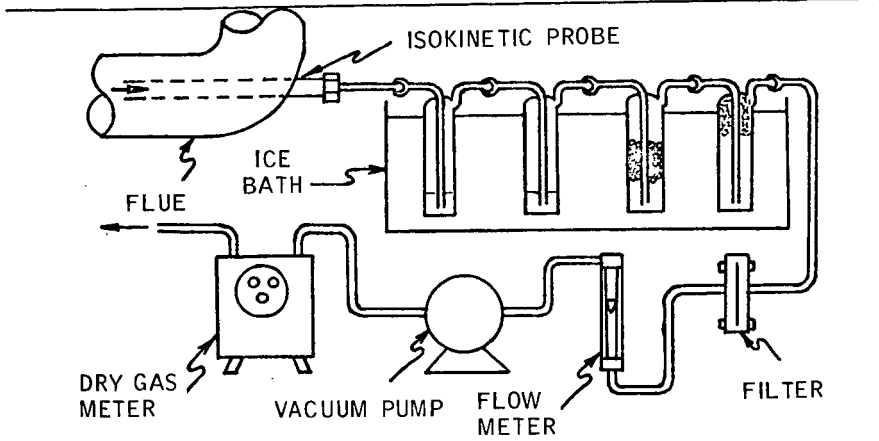
FIGURE 1

PNA SAMPLING SYSTEM
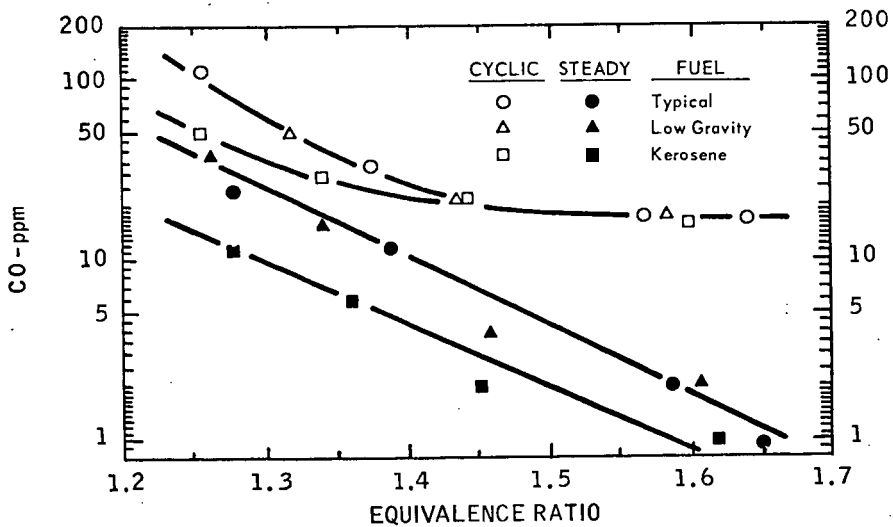

FIGURE 2
CARBON MONOXIDE EMISSIONS
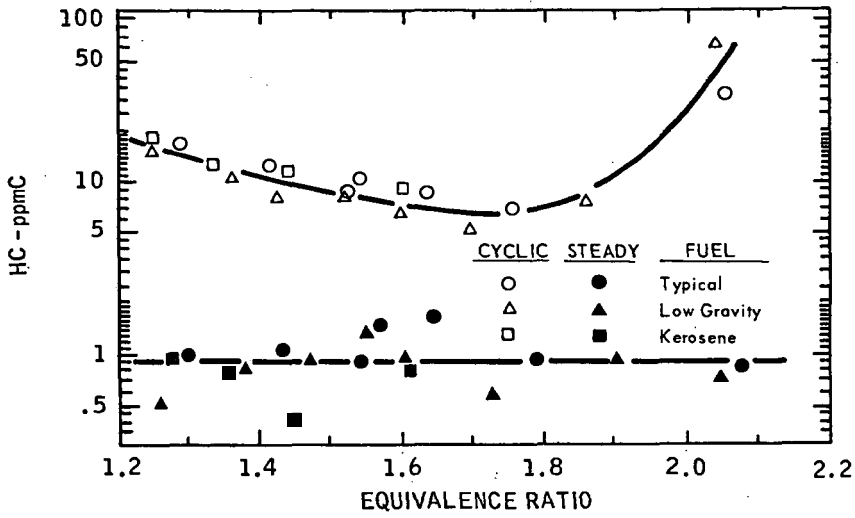
FIGURE 3
HYDROCARBON EMISSIONS

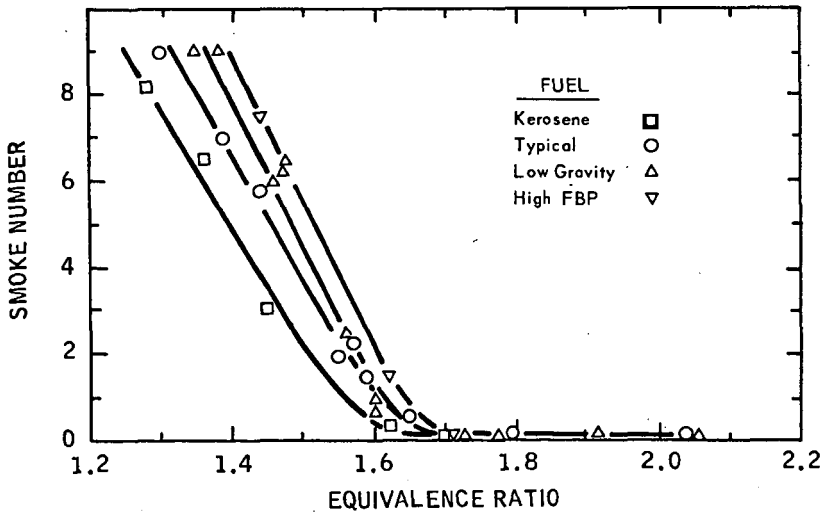FIGURE 4
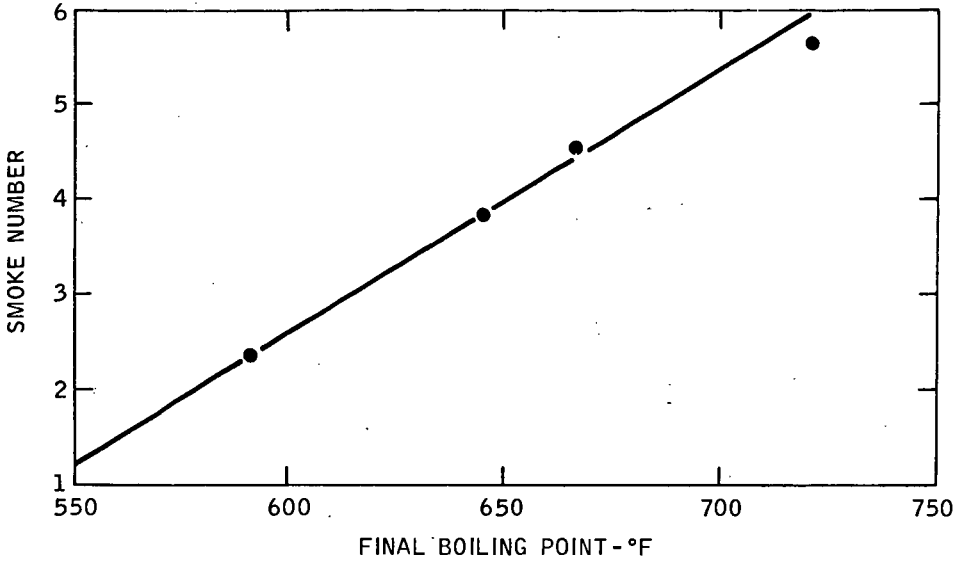FUEL EFFECT ON SMOKE NUMBER

FIGURE 5

INFLUENCE OF FINAL BOILING POINT OF FUEL ON SMOKE

FIGURE 6

PARTICULATE EMISSIONS